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# SYNTHETIC ORGANIC CHEMICALS

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## Synthetics Used in Perfumery

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THE organic substances that are extensively used in perfumery comprise one of the most fascinating groups of synthetic compounds. They have relatively simple molecular structures as compared to the vitamins and hormones; their general chemistry has been well worked out and much of it is recorded in the literature. However, some of the newer developments are particularly interesting and therefore will be briefly discussed in this article and another which will follow in an early issue of SYNTHETIC ORGANIC CHEMICALS.

The simplest type of compound, and perhaps the best known, comprises the esters of aliphatic acids and alcohols of small molecular weight. The common acid radicals, from formate to valerate, are esterified with the corresponding alcohols, methyl to amyl, to form compounds whose fruity odors are easily recognizable. The less common higher alcohols, octyl to lauryl, form esters whose odors range from a fruity (orange) to a flowery (rose) fragrance, and are so powerful that only small quantities are usually required.

Most of the esters containing an aromatic group are familiar substances and include the benzoates, salicylates, anisates, phenylacetates, anthranilates, and derivatives of benzyl alcohol. Less well known are the derivatives of phenylethyl alcohol which, like the alcohol, have a

rosy odor; the group of tertiary alcohols and esters obtained by Grignard reactions; and the styralyl series. The methods of preparation of the two latter groups deserve brief mention.

Phenylethyl alcohol is obtained either by the interaction of phenylmagnesium chloride and ethylene oxide or by the reduction of ethylphenyl acetate, which is itself a perfume ingredient. Other tertiary alcohols in a homologous series, such as dimethylphenyl, dimethylbenzyl, phenylethyldimethyl, and phenylethylmethylethyl carbinols, are obtained by the Grignard reaction. Anisyl alcohol (*p*-methoxybenzyl alcohol) and cinnamyl alcohol are produced by the reduction of the corresponding aldehydes. The esters of the styralyl series are the bases of various gardenia perfumes. Their naming is confusing, however; phenylmethyl acetate is really phenylmethyl carbonyl acetate—

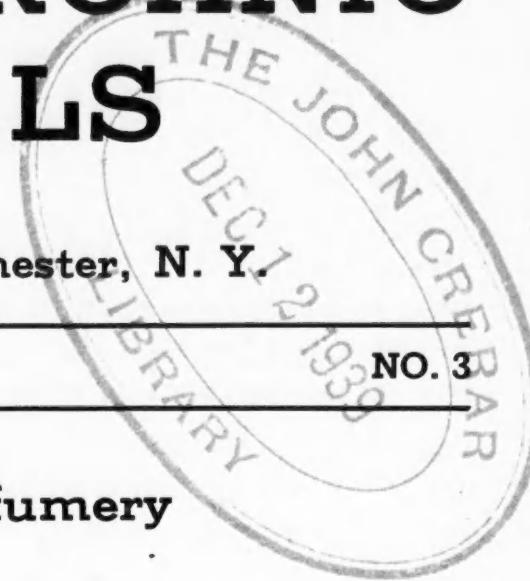


while styralyl acetate is

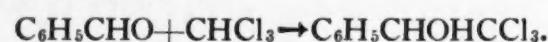


The corresponding styralyl diacetate finds limited use.

Certain of the higher boiling esters have little or no odor, but are valuable as fixatives. A fixative is a substance added to a perfume to prevent too rapid volatilization of its various components; it blends them into a more lasting fragrance. Included in this group of com-



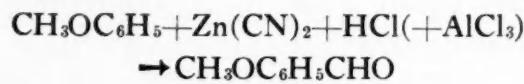
pounds, which are frequently good solvents for the nitromusks, are benzyl benzoate, phenoxyethyl alcohol, and phenyltrichloromethyl carbonyl acetate which has a very faint rosy odor. The phenyltrichloromethyl carbinol from which the last is made is obtained by an unusual reaction—



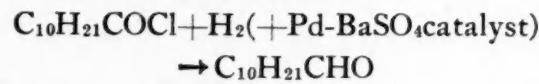
Aldehydes, ketones, and ethers are valuable oxygen-containing substances. Only a few of the ethers are used, but they are very stable substances and non-irritating to the skin; diphenyl ether,  $\beta$ -naphthylmethyl ether, and hydroquinonedimethyl ether are the ones most commonly employed.

The value of aldehydes lies in their use not only as ingredients, but also as chemical intermediates for the preparation of more complicated substances. Benzaldehyde, vanillin, piperonal, cuminaldehyde, phenylacetaldehyde, and the common aliphatic aldehydes are described in most textbooks, which also give general methods for their preparation. In addition to isolating these compounds from natural products, many synthetic methods are now employed. The more recent of these include:

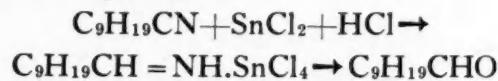
Adams' modification of the Gatterman reaction—



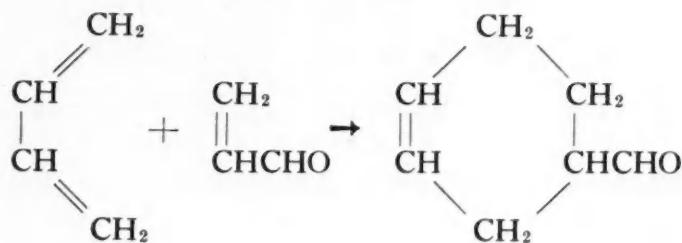
Rosenmunde's reaction—



Stephen's synthesis—

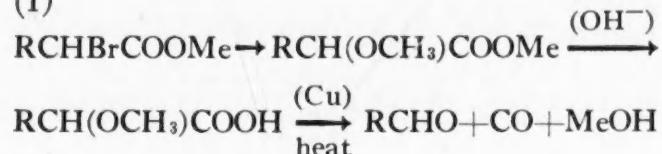


Diels-Alder diene synthesis, which is capable of great variations (See SYNTHETIC ORGANIC CHEMICALS, Vol. X, No. 5, Dec., 1937)—

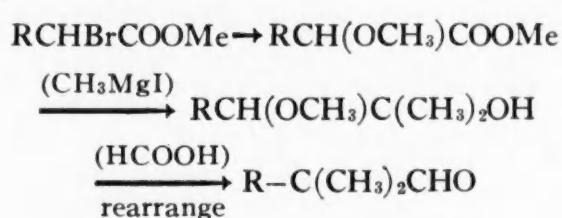


and Darzens' procedures. These are summarized by the following scheme from which it will be noted that there are two types of aldehydes obtainable—

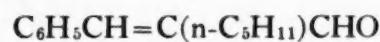
(I)



(II)

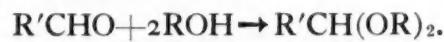


The aldol condensation reaction, using n-heptaldehyde and benzaldehyde, results in the formation of  $\alpha$ -n-amyl cinnamic aldehyde—



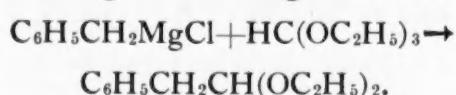
an important compound employed as a substitute for indol in some jasmine perfumes. The higher aliphatic aldehydes having from 9 to 12 carbon atoms possess such powerful odors that only traces of them are required in a perfume. An example of the effect of a branched chain on the odor is noted in two dodecyl ( $C_{12}$ ) aldehydes, the straight chain lauric and the branched chain methyl-nonyl acetaldehyde being quite different. "Cyclamen" aldehyde is chemically p-isopropyl- $\alpha$ -methyl hydrocinnamaldehyde; ethyl vanillin is the ethoxy analog of ordinary vanillin.

The ease of auto-oxidation of aldehydes has resulted in many attempts to increase their stability. It has long been known that aldehydes in alcoholic solution were more permanent and this has been traced to hemi-acetal formation. Consequently, acetals, which contain an ether-like linkage, were introduced, but their odors, though valuable, were seldom found to be the same as those of the original aldehydes. A general synthesis may be represented as—



In addition they may be obtained di-

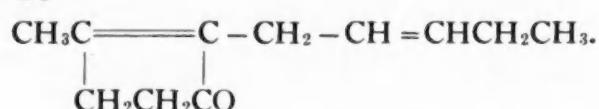
rectly through the Grignard reaction—



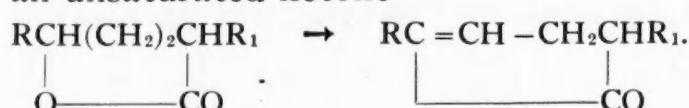
Since acetals are easily hydrolyzed, this reaction furnishes an additional method of securing aldehydes.

Among the ketones which have been found valuable in perfumery may be mentioned benzalacetone,  $\beta$ -naphthylmethyl ketone, acetophenone, jasmone, and the musks. The first three are obtained by familiar reactions.

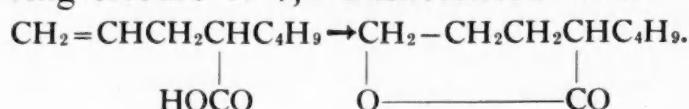
Through brilliant research culminating in its synthesis, Treff and Werner determined the constitution of jasmone to be—



As a result of this work, a series of analogous odorous ketones have been synthesized and are now available for practical use. In addition to the aldol condensation type reactions and the usual ring closure methods, a novel procedure which involves heating lactones with activated infusorial earths has been developed for the preparation of ketones. A molecule of water is lost, resulting in an unsaturated ketone—



The necessary branched chain cyclic lactones are formed by the intramolecular ring closure of  $\gamma, \delta$ -unsaturated acids—



## Eastman Organic Chemicals as Analytical Reagents

### XLVII REAGENTS FOR SELENIUM

#### 1,8-DIAMINONAPHTHALENE

Feigl, *Qualitative Analysis by Spot Tests*, 216

When a solution of selenious acid or alkali selenite is heated with an acetic acid solution of 1,8-diaminonaphthalene, a brown insoluble precipitate is formed. In the absence of nitrites, the reaction is specific for selenites and will detect 1 part in 50,000.

A drop of the test solution, neutral or slightly acid, is mixed with 1-2 drops of a 0.5% solution of the reagent and a drop of acetic acid added. The tube is placed in boiling water for 5-10 minutes. A light or dark brown precipitate forms, depending upon the amount of selenite present.

#### THIOUREA

Denigès, *Bull. soc. pharm. Bordeaux*, 75, 197 (1937)

Thiourea reacts with selenite ions to form a red precipitate. One drop of 5% aqueous thiourea and 1 drop of N HCl are added to a small sample of the unknown. Selenate ions show a precipitate only after several minutes while the

reaction is immediate with selenite ions.

In testing natural water, a 60 cc. sample is evaporated to 4 cc., 5 drops of HCl added, the solution made to 6 cc. and filtered. To 5 cc. of the filtrate are added 2 drops of HCl and 5 drops of the reagent, which is then boiled and cooled for 5 minutes. The presence of 0.05 mg. of selenium per liter produces turbidity.

#### PYRROLE

Berg & Teitelbaum, *Mikrochemie, Emich-Festschrift*, 23 (1930)

Under suitable conditions, selenious acid oxidizes pyrrole to a blue dye-stuff of unknown constitution. To a drop of the test solution are added a drop of a 5% ferric chloride solution and 7 drops of syrupy phosphoric acid, and the mixture stirred. One drop of a 1% alcoholic solution of pyrrole is then added and the mixture again stirred. A green-blue color indicates the presence of selenious acid. Iron salts do not interfere nor do selenic, tellurous, or telluric acids react, making it possible to distinguish between selenic and selenious acids.

## Eastman Organic Chemicals

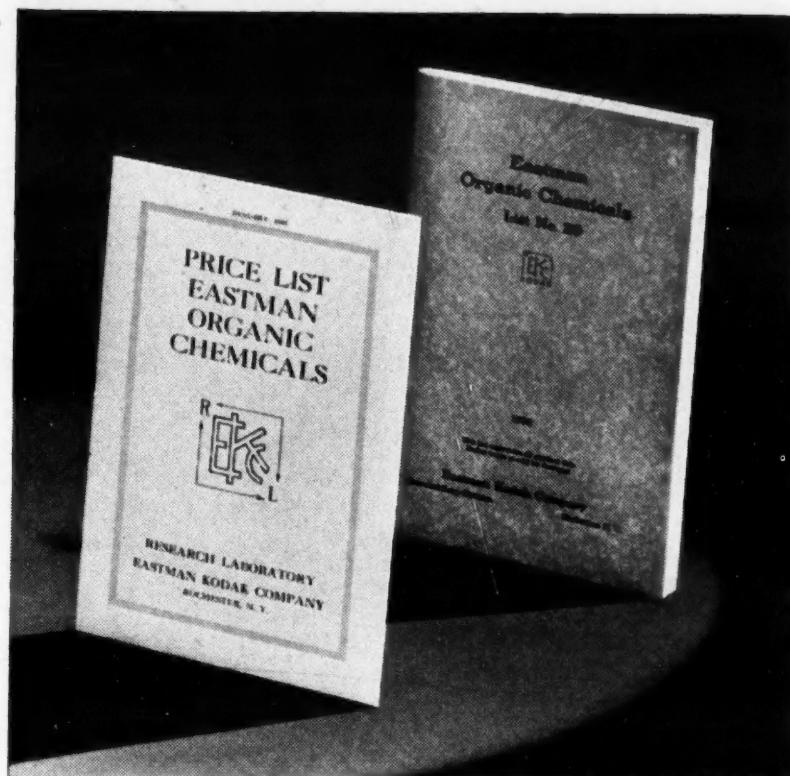
**T**HE 29th edition of the catalog of Eastman Organic Chemicals was issued in May. Twenty years ago, the production of these chemicals was begun in a special department of the Kodak Research Laboratories in order "to insure the complete independence of this country in regard to those materials which are essential to the advancement of chemical knowledge." How well this original objective has been attained is shown in the illustration of the first and latest chemical price lists.

Perhaps more graphic than the photograph are a few figures. List No. 29, of May, 1938, is an impressive 124-page book cataloging 3,180 different chemicals, the largest group of organic chemicals in the world. Over 350 of these items are supplied in more than one grade for a total listing in excess of 3,500. List No. 1, a 4-page leaflet published in January, 1919, contained less than 150 items. This increase of more than 3,000 compounds means the addition of an average of 150 new chemicals per year.

The present list contains 99 items which have not appeared before. The great variety of these new chemicals makes them of interest to chemists in all branches of research.

For the biochemists, the amino acids form an important type; the extensive group carried has been augmented by the addition of the following four new acids—*β-alanine*, *ε-amino-n-caproic acid*, *dl-serine*, and *dl-threonine*.

*Cellulose acetate propionate*, *cellulose acetate butyrate*, *cellulose acetate stearate*, and *cellulose acetate hydrogen phthalate* are examples of the new cellulose mixed esters which are receiving considerable attention. The last is especially interesting because of the novel characteristics resulting from its acidic character. Al-



*The first list of Eastman Organic Chemicals (left) consisted of four pages—List No. 29 (right) contains one hundred and twenty-four.*

though it is insoluble in water, it may be converted by alkaline reagents into water-soluble salts.

The majority of the new compounds are valuable to organic chemists engaged in synthesis. Deserving of special mention are the ortho esters, two more of which, *ethyl orthoacetate* and *ethyl orthoformate*, are now available.

For analytical chemists, the new reagent, *neocupferron*, is offered. *Naphthaleneacetic acid*, which has been recommended for the stimulation of root growth on plant cuttings, is now furnished in a purified grade.

Improved methods and lower costs of raw materials have had the advantageous effect of making possible more than 350 price reductions. In only a few cases have special conditions necessitated slight increases. The past twenty years have been productive of remarkable advances in the field of organic chemicals. It is our hope that we may continue our part in making the future years equally as progressive.